

Acid activation of Bentonite for use as a vegetable oil bleaching agent

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RESUMEN

Activación ácida de Bentonita para ser usada como agente decolorante de aceites vegetales.

Se describe el empleo del diseño de experimentos con objeto de evaluar y simular los efectos de la activación ácida de bentonita procedente de Argelia en la decoloración de aceite de colza. Para ello se evaluaron tres variables: concentración de ácido, tiempo de contacto y temperatura. Empleando como variable respuesta la efectividad en el proceso de decoloración, los resultados obtenidos indicaron que las tres variables proporcionaban un efecto beneficioso hasta un determinado nivel, siendo la concentración de ácido, el factor que producía una mayor variación en la variable respuesta. Se observaron pequeñas interacciones entre los efectos estudiados. Se obtuvo un 99 % de capacidad para la decoloración como valor óptimo. El tratamiento estadístico realizado indicó la presencia de un efecto sinérgico. Una activación excesiva se puede explicar en términos de una pérdida de porosidad y fuerza ácida.

PALABRAS CLAVE: Activación ácida – Bentonita – Diseño de experimentos – Decoloración de aceite.

SUMMARY

Acid activation of Bentonite for use as a vegetable oil bleaching agent

The design of various experiments in order to assess and simulate the effects of the acid activation of an Algerian bentonite on the bleaching capacity of Colza oil is described. Three key parameters of the acidic activation, namely acid concentration, contact time and temperature, were considered. The calculations made indicated that all variables display advantageous effects up to a certain level on the effectiveness of bleaching, regarded as the response-function. The acid concentration exerts a predominant individual effect as compared to the other parameters. Some small interactions between parameters were considered. High bleaching capacity reached 99% as optimal activation. Under accurate statistical measurements, synergy phenomena could be observed. Excessive activation is discussed in terms of loss in both porosity and acid strength.

KEY-WORDS: Acid activation – Bentonite – Design of experiments – Oil bleaching.

1. INTRODUCTION

Acid-activated clays are the most common bleaching agents for vegetal oils. Among them,

activated bentonites are regarded in bleaching industries as references for removing chlorophyll, carotenoids, phospholipids, metals and oxidation products from oils. So far, the removal of these constituents has been explained only in terms of adsorption (Kheok and Lim, 1982; Taylor *et al.*, 1989), but the interactions occurring between the activated clay and dispersed oil components, more particularly with organic compounds, is more complicated and needs further research.

For instance, in the presence of metal cations in water, the interaction of montmorillonite with chitosane involves a complex coagulation-flocculation process that includes not only absorption, but also chelation and ion-exchange (Assaad *et al.*, 2007). A series of features including the available surface area and acidity of the clay sheets, along with the exchangeable cations exert influence upon the bleaching capacity of a given clay (Güler and Tunç, 1992; Liew *et al.*, 1982; Taylor and Jenkins, 1988). Some authors reported that the acidity of the clay surface seems to enhance the adsorption of β -carotene from acetone (Liew *et al.*, 1982) and chlorophyll from hexane (Güler and Tunç, 1992) into the clay. Nonetheless, unless traces of water are present in the oil to be treated, their attempts to explain the role of the acidic sites in dry media were not satisfactory, inasmuch as acid-base interactions similar to those occurring in gaseous phase are involved (Azzouz *et al.*, 2006).

Clay features are strongly dependent on the activation procedure. Acid treatment is expected to improve the specific surface area and porosity, unless the clay framework collapses, more particularly under severe activation conditions. Nonetheless, the decay in bleaching effectiveness cannot be explained in terms of clay structure collapsing only, as reported by some authors (Kheok and Lim, 1982), since in our view, high specific surface area and porosity do not necessarily give rise to high bleaching activity in the clay. Indeed, even in the absence of framework destruction, the acidic activation of bentonites must involve partial delumination, inducing an increase in the silica/alumina ratio. As a result, there will be an increase in the number of weak acidic Si–OH groups and subsequently in the global acidity of the clay's surface, though only up to a certain level.

Nevertheless, this may occur at the expense of not only [Si–O–Al]H groups in the tetrahedral layers of the clay lamellae, if traces of beidellite are present, but also most of [Al–O–Metal²⁺]H groups, in the case of an extensive acid attack on the octahedral layer in montmorillonite. These removed groups are well known for displaying stronger acidities than terminal silanols (Azzouz *et al.*, 2006) and are presumably involved in absorption sites (Taylor *et al.*, 1989). Consequently, both the acidity strength and negative charge of the clay surface will rather decrease, in contrast with results reported by these authors (Kheok and Lim, 1982). Furthermore, high pore volume seems to play a predominant role within the total volume pore.

Therefore, any variation of the activation parameters has a great impact upon the distribution of the acid strength and of the pore volume of the clay material. This is why full control of the bleaching capacity of a given clay material requires a thorough understanding of the role of activation parameters for a hierarchical ranking of their influences. This can lead to an accurate compromise between highly accessible surface areas with a high number of sites that interact with the dispersed oil components.

In this context, the design of experiments using statistical measurements turns out to be a judicious route for processes that do not obey well-defined deterministic models. Although it seems to be a good alternative, the use of factorial experimental designs has scarcely been envisaged in this regard, most of the experiments being dedicated only to the optimization of clay activation (Didi *et al.*, 2009; Kirali and Laçin, 2006). So far, no statistical approach has been considered so as to correlate parameters that control clay activation for effective oil bleaching processes and neither factors, interactions or synergy have been discussed. To such an end, based on the results obtained in a previous work using a factorial 3³ experimental design (Didi *et al.*, 2009), calculation attempts were made to assess and simulate the effects of the following three key parameters on the bleaching capacity of an Algerian bentonite in the colza oil processing: acid concentration, contact time and temperature.

2. MATERIAL AND METHODS

2.1. Materials and equipment

In these trials, a bleaching earth for colza oil processing was obtained through the acid-

activation of a bentonite originating from Maghnia (Algeria). The mineralogical analysis showed that the native crude clay mineral contains preponderantly Montmorillonite (85%) (Makhoukhi *et al.* 2008).

Pretreated, neutralized, washed and dried colza oil was supplied by ENCG Co. (Algeria). Measurements of Yellow and Red colors of the oils (bleached and unbleached) were performed on a Lovibond Tintometer (Model E–AF 710-2) using a 5^{1/4} inch cell (European Journal of Lipid Science and Technology, 2001).

2.2. Acid activation

A fine bentonite suspension in water (320 g dry clay per liter) was put in contact with pure H₂SO₄ (98%) at various temperatures (60–120 °C), for various contact times (6–12h), as reported elsewhere (Didi *et al.*, 2008). After activation, the solid residue was filtered, repeatedly washed with distilled water until reaching a neutral pH, and then at 100 °C for 6h or overnight at 40 °C. Then the dried bentonite was crushed to a particle size that would pass through a 75 µm sieve (200 mesh ASTM).

2.3. Experiment Design around the central point for Colza oil bleaching

The present study comes to pursue a previous work dealing with the optimisation of the bleaching capacity (Didi *et al.*, 2009). Therefore, based on a series of 27 attempts made according to a 3³ experiment factorial design, by varying the acid concentration (X₁), the contact time (X₂) and the temperature (X₃) in suitable parameter ranges, calculations were made in order to assess the estimated standard deviation of the model as a response-function. Three variation levels for each parameter were considered (Table 1).

The bleaching attempts were performed in a round-bottom three-necked flask equipped with a stirrer, a contact thermometer and a three-way valve (used to apply or break the vacuum).

A mixture of 1g of dry activated bentonite and 100 g of oil was heated under continuous stirring at 100 °C, for 20 min. The contact time between oil and bleaching earth should not exceed 20 min at 100 °C to avoid undesired side-reactions (European Journal of Lipid Science and Technology, 2001).

After oil treatment, the bleaching earth was removed by filtration. Prior to color change

Table 1
Factor levels used in the 3³ factorial experiment design at (S/L) ratio = 320 g/L

Factors	Symbol of coded Variables	Low level (-1)	Medium level (0)	High level (+1)
Acid concentration (%)	X ₁	28	32	36
Contact time (h)	X ₂	4	6	8
Temperature (°C)	X ₃	60	90	120

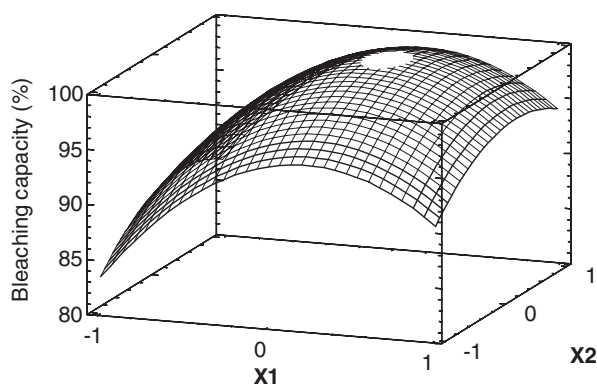


Figure 1
3D representation of the bleaching capacity
of activated bentonite at fixed $X_3 = 0$
 X_1 : acid concentration; X_2 : activation time.

measurements, care should be taken that the filtrate is thoroughly clear.

Color changes in the treated oils were assessed through spectrophotometry by means of a Perkin Elmer–Lambda 800 instrument in terms of transmittance at the following wavelengths: 510, 540, 580 and 610 nm. Triplicate measurements were required to accurately determine the bleaching capacity of the activated bentonites by comparison with a standard bleaching earth (Optimum Tonsil- Germany). The bleaching capacity of the activated bentonites was expressed in terms of average [activated bentonite: standard] transmittance ratio (%).

A special feature of purified colza oil is its low chlorophyll content expressed in ppm. The latter was estimated by measuring the absorbance of the bleached oil sample at 630 nm, 670 nm and 710 nm at 30 °C, using a spectrophotometer (UNICAM) and carbon tetrachloride as reference (AOCS–Method Cc 8b-52, 1979).

3. RESULTS AND DISCUSSION

3.1. Experimental design for colza oil bleaching

Preliminary observations show that bleaching capacity varies significantly according to the experiment parameters, reaching values of 98–99% under certain operating conditions. A clear evidence for the judicious choice of the parameters range is that the highest bleaching capacity is obtained around the middle of the considered ranges, as shown in Table 2. Indeed, for an average acid concentration of 32%, and an average activation time of 6 hours, the bleaching capacity reaches values of 98.1–98.87%. According to these data, it appears that the temperature and all parameter interactions exert very weak effects over the bleaching capacity around the middle of the considered parameter ranges.

This is why a special interest should be focused towards those attempts involving mean values of the key-variables.

Such 3^k factorial designs, implying three variation levels, have already proven their effectiveness in some studies (Assaad *et al.*, 2007; Bodo *et al.*, 2004) because they need only one single set of experimental attempts to assess both the single effect coefficients and the quadratic terms, in contrast with those of type 2^k with two variation levels. The latter require two separate set of experiments (Kiralı and Laçın, 2006). This may affect the calculation accuracy and the reliability of the conclusion, especially when dealing with the correlation between the response-surface curvature and the parameter interactions.

3.2. Model calculations and adequacy tests

The modeling of the bleaching capacity is based on the 27 measured values, using a Taylor's second-order polynomial (Bodo *et al.*, 2004). The model calculations were achieved using non-dimensional or reduced values of these variables, each of them being changed on three levels. The following mathematical model shows the values corresponding to each coefficient of the model ($b_i = b_0, b_1, b_{10}$), supposed to describe the individual effects of parameters, along with their possible interactions.

$$Y = 98.87 + X_1 + 1.78 X_2 + 0.24 X_3 - 0.64 X_1 X_2 + 0.09 X_1 X_3 - 0.03 X_2 X_3 - 14.05 X_1^2 - 2.8 X_2^2 - 0.7 X_3^2 - 0.17 X_1 X_2 X_3 \quad (1)$$

The model adequacy strongly depends on the accuracy of the experiment. In the current experiment, the main errors come from volume and weight measurements. The fact that the optimum activation parameters are included within the considered variation ranges confirms once again the judicious choice of these ranges and the applicability and accuracy of the model developed in this study. Under these conditions, the calculated bleaching capacity reaches a maximum value of 98.87%. Additional bleaching attempts at the optimum activation parameters revealed experimental bleaching capacities of nearly 99%, very close to the calculated value. Despite this, adequacy tests remain as yet strongly recommended to check whether the calculated model is valid within the range of the investigated parameters (Assaad *et al.*, 2007; Bergouzini and Duby, 1995; Bodo *et al.*, 2004). For this purpose, three additional attempts at the central point (0, 0, 0) are required for estimating the average error in the value of each coefficient, on the basis of the random variance. Calculation details are summarized in Table 3. A first adequacy test showed that d , the discrepancy between the average bleaching capacity value, $y_0 = 98.5$, and the model response for the three additional attempts at the (0, 0, 0) point is smaller than Δd , indicating that

Table 2
Experimental design and bleaching capacity of activated bentonite

Experiment no.	Factors levels			Response function
	X_1	X_2	X_3	(%) Bleaching capacity
1	-1	-1	-1	66.85
2			0	67.06
3			1	66.90
4		0	-1	71.90
5			0	73.20
6			1	72.60
7		+1	-1	71.70
8			0	72.80
9			1	72.20
10	0	-1	-1	94.30
11			0	94.90
12			1	94.50
13		0	-1	98.10
14			0	98.87
15			1	98.32
16		+1	-1	96.90
17			0	97.60
18			1	97.10
19	+1	-1	-1	91.50
20			0	93.10
21			1	92.80
22		0	-1	96.10
23			0	97.20
24			1	96.80
25		+1	-1	94.70
26			0	95.80
27			1	95.10
(28, 29, 30) ^a	0	0	0	98.15, 98.5, 98.85

^a Three additional tests at the central point (0, 0, 0) for the calculation of the student's *t* test.

the model can be quite valid within the entire range considered in this study

On the basis of a *t*-student factor of 4.3, corresponding to a 95% confidence and a variance equal to 2 (i.e., for three attempts at the central point), the coefficients b_3 , b_5 , b_6 and b_{10} will have smaller values than even their own assessment error. For optimization, these coefficients can be omitted, but they could be very useful for the simulation of effects. The resulting new model will be the following:

$$Y = 98.87 + 12.11 X_1 + 1.78 X_2 - 0.64 X_1 X_2 - 14.05 X_1^2 - 2.8 X_2^2 - 0.7 X_3^2 \quad (2)$$

Both the individual effects and interactions of the parameters were discussed on the basis of the sign and the absolute value of each coefficient. These coefficients define the strength of the corresponding effect involved and the way it acts upon bleaching capacity (favorable or detrimental). This mathematical model lead to the following remarks:

1. The general tendency is that all the three considered activation parameters display favorable individual effects on the bleaching capacity of the used bentonite, but with different strengths.
2. As expected, the individual effect of the acid concentration is almost stronger than that of the activation time, yet by far higher than that of the temperature.
3. The parameter interactions appear to be relatively weak as compared to the individual effects.
4. The interaction between the acid concentration and activation time seems to hinder the bleaching capacity.
5. All interactions are detrimental, except those between the acid concentration and temperature.

3.3. Parameter optimization

From the above polynomial model, the highest bleaching capacity was obtained with a bentonite

Table 3
Model adequacy tests at (0, 0, 0) point and Student's *t* test

Feature	Symbol	Value	Results
Model variance	v	2	t-student test: $ \Delta b_i > b_i $ these coefficients must be removed from the model, because their corresponding effects are considered very weak with a 95% confidence
Average bleaching capacity at (0,0,0) point	y_0	98.5	
Random variance	S^2	0.122	
Square root of variance	S	0.35	
Risk factor (chosen arbitrary)	α	0.05 (95%)	
Student's <i>t</i> test factor	$T_{v, 1-\alpha/2}$	4.3 *	
Average error on the coefficient value (trust range)	Δb_i	± 0.289 at 95%	
Number of remaining coefficients	R	7	1 st method of model adequacy $ d < \Delta d $ with a 95% confidence **
Model response at (0,0,0)	$b_0 (y_{000})$	98.87	
Discrepancy on average yield	d	0.37	
Error on average yield discrepancy	Δd	± 0.915	
Average yield for the 27 attempts	Y_m	87.36	2 nd method of model adequacy $F \gg F_{0.95, 3}$ with a 95% confidence
Residual variance	S_r^2	207.17	
Degrees of freedom	v_1	3	
Residual degrees of freedom	v_2	4	
Fisher test	F	592	
Fisher-Snedecor Law	$F_{\alpha, v_1, v_2}^{***}$	$F_{0.95, 3, 4} = 6.6$	

* Student Law with 2 degrees of freedom at a 95% confidence ($t_{2, 0.975}$).

** After removing the less significant coefficients.

*** See Fisher-Snedecor tables.

whose activation was performed at average values for acid concentration, activation time, and temperature (Table 2). Graphical determination (Fig. 1) was achieved both by calculations and by using 2D representation of the bleaching capacity as a function of the acid concentration and activation time, maintaining constant the temperature at its average value, assumed to be in the vicinity of the optimum value.

A more precise method for determining the optimum parameter values consists of the derivation of the polynomial model. Table 4 summarizes the obtained results. Both methods lead to the same results, confirming that neglecting the effect of the third factor, namely the temperature does not affect the accuracy of the model.

It should be duly noted at this point that the optimization calculations gave values that lied within the respective selected ranges (Acid concentration = 34% and contact time = 6.5h), confirming once again the judicious choice of the parameter ranges and the applicability and accuracy of the developed model in order to describe the correlation between the bentonite activation factors and its performances in colza oil bleaching. Under these conditions, a bleaching capacity value of 98.90% was obtained.

Few additional attempts, performed around the calculated X_{opt} values, revealed that high bleaching capacity values around 99% can be reached for the following: Acid concentration = 34%, contact time = 7h and temperature = 90 °C. These experimental data agree with the calculated data. In our opinion, these results are satisfactory, with no further need for additional factorial design with more severe activation parameters, since a more concentrated system or prolonged activation time are not strongly recommended.

3.4. Assessment of the optimum activation parameters

The bleached colza oil treated with 1% of the activated bentonite sample that displayed the highest effectiveness was fully characterized and the results were compared to those obtained with an optimum Tonsil bleaching earth (Table 5).

The results analysis indicated that chlorophyll was almost completely adsorbed into the activated bentonite, with traces lower than the recommended threshold at present.

The acid-activated clays have strong Lewis and Brönsted acid sites. As a result of an acid-base

Table 4
Optimum activation parameters for highest bleaching capacity

Parameter	Coded variable	Non dimensional values	Real optimum values
Acid concentration	X_1	0.425	34 %
Activation time	X_2	0.27	6.5 h
Temperature	X_3	0	90 °C

Table 5
Colza oil analysis before and after bleaching

Bleaching earth Sample	Purity criterion ^a	Dry colza oil	
		before bleaching	after bleaching
Activated bentonite	Chlorophyll (ppm)	3.40	0.038
	Color tests: yellow Red	50 5	18 2
Tonsil Optimum (reference)	Chlorophyll (ppm)	3.40	0.038
	Color tests: yellow Red	50 5	16 2

^a Recommended values: Chlorophyll < 0.040 ppm, Color tests: < 20 for yellow ; < 2 for red.

reaction, the adsorption of chlorophyll into acid-activated clay occurs and seems to be mainly a chemical process stemming from the interaction of chlorophyll with the Lewis and Bronsted acid sites of the clay (Liew *et al.*, 1982).

Simultaneously, color tests gave values of 18 for yellow and 2 for red, which are included within the recommended range, confirming thereby the high efficiency of the bleaching process using bentonite samples activated following the optimized procedure. The highest performance, corresponding to ca. 99% of bleaching capacity was obtained with only 1wt % of the same bentonite. This result is of a great importance for continuing the investigation in this regard, because our activated bentonite exhibited the same performances as those of the Tonsil optimum, requiring less amount of bentonite for similar bleaching capacities.

These results can be expected if one takes into account that increasing all the three parameters will lead to severe acid-attack and pronounced dealumination. This may affect not only the clay porosity by possible framework deterioration, but also the strength of the surface acidity. In the total absence of bedelilite, in montmorillonite the number of silanol groups is not expected to increase significantly, most of them being restricted to those already existing at the edge of the clay lamellae. Consequently, the decrease in the acidity strength will be attributed only to a decrease in ([Al-O-Metal²⁺] Cations) sites, as a result of dealumination. Nonetheless, protonation of the remaining ([Al-O-Metal²⁺] Cations) must be neglected at these acid concentrations (Azzouz *et al.*, 2006).

The occurrence of optimal activation parameters (Didi *et al.*, 2009), beyond which a decay of the bleaching capacity takes place, is clear evidence that activation improves the surface area, porosity and acidity of the clay material, but only up to a certain level. The fact that dealumination of the clay minerals and protonation of the ion-exchange sites occur inevitably upon acid-activation reveals that high bleaching capacities require acid sites stronger than silanol groups and the remaining protonated ([Al-O-Metal²⁺]H) sites. If one takes into account that protonated exchangeable sites ([Al-O-Metal²⁺]H are

weaker in acidity than the ([Al-O-Metal²⁺]) cations (Azzouz *et al.*, 2006), then the presence of multivalent cations is an essential requirement for higher bleaching activities, in agreement with previously reported data (Güler and Tunç, 1992; Liew *et al.*, 1982). A possible explanation should consist of the polarizing effect of multivalent cations. The latter ought to induce not only water molecule dissociation and then Bronsted sites with releasable protons, but also electrostatic fields on the clay surface. The occurrence of such electrostatic fields is presumably the cause of molecule attraction and adsorption. Such a phenomenon must be very similar to coagulation-flocculation processes in water (Assaad *et al.*, 2007), or gas adsorption in dry media (Azzouz *et al.*, 2006).

Therefore, adsorption on the ion-exchange sites must involve not only their strong acidity (Taylor *et al.*, 1989) but also their partial charges. Their disappearances upon acid-attack will inevitably affect the bleaching capacity, even if the surface area and porosity are preserved because both acidity strength and the negative charge of the clay surface will decrease. This is why a full control of the activation parameter must imply small variation ranges for parameters displaying strong individual effects and vice-versa. When detrimental, a parameter interaction has to be hindered by operating at the lowest values of the corresponding parameters, as in the case of the combined effect of acid concentration and activation time. Conversely, when advantageous, a parameter interaction must be enhanced by performing activation at the highest value parameter, like for the interaction involving the clay to oil ratio and the acid concentration or the activation time.

4. CONCLUSIONS

Optimized acid treatment of the Algerian bentonite gave rise to an effective bleaching earth in colza oil treatment. The highest bleaching capacity and a model for acid activation of bentonite were investigated by means of 3³ factorial design. The result presented herein provides clear evidence that

the acid concentration and activation time influence greatly the bleaching capacity of bentonite, while the temperature exerts no significant individual effect on the activation of bentonite. The investigated parameters also exert binary interactions that must not be neglected. The highest bleaching capacity was found to be ca 99%, under optimum activation conditions, namely: acid concentration (34%), contact time (7 h) and temperature (90 °C). The polynomial model developed herein for the bleaching capacity of oils may provide a valuable basis for industrial scale applications.

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